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## TECHNICAL NOTE No. 5

SPECTROSCOPIC STUDIES: PART 2, THE INFRA-RED SPECTRA  
AND STRUCTURE OF METHOXYACETONITRILE  
AND METHYL-CHLOROMETHYLETHER

R. G. Jones and W. J. Orville-Thomas

THE EDWARD DAVIES CHEMICAL LABORATORY

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*List of Technical Notes*

- TN-1 : Force Constants in Boron Trihalides. June, 1963.
- TN-2 : Infra-red Dispersion Studies : Part 1, Dichloro-, Dibromo-, and Diiodomethane.  
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- TN-3 : Vibrational Frequencies and Electronegativities. June, 1963.
- TN-4 : Spectroscopic Studies : Part 1, The Infra-red Spectrum and Structure of Sodium Nitro-  
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- TN-5 : Spectroscopic Studies : Part 2, The Infra-red Spectra and Structure of Methoxyacetonitrile  
and Methyl-Chloromethylether.

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## **TECHNICAL NOTE No. 5**

### **SPECTROSCOPIC STUDIES: PART 2, THE INFRA-RED SPECTRA AND STRUCTURE OF METHOXYACETONITRILE AND METHYL-CHLOROMETHYLETHER**

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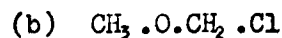
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The infra-red spectra of methoxyacetonitrile and methyl-chloromethyl-ether have been studied in solution and in the vapour and liquid states.

In the vapour state the band contours prove that the molecules are most stable when they have a slightly twisted trans conformation.

Methoxyacetonitrile (a) and methyl- chloro- methyl-ether (b) differ only in that the nitrile group of one is replaced by a chlorine atom.



Since the nitrile group and the chlorine atom have approximately the same electronegativity and mass it is reasonable to expect that the vibrational frequencies of the  $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2$  - group will change but little in going from (a) to (b).

In both molecules rotation about the  $(\text{CH}_3) \text{O} - \text{C}(\text{H}_2 \text{X})$  bond is possible. (Fig. 3.) In their most stable states the molecules will have particular conformations corresponding to certain definite values for the moments of inertia. A study of the band contours, obtained from vapour phase spectra, then, should give a reliable indication as to the most stable conformation.

Methyl chloromethyl ether, together with the corresponding thio-ether, has been studied by Hayashi.<sup>2</sup> The Raman spectra of (a) and (b) have been recorded.<sup>2,3</sup>

## EXPERIMENTAL.

Methoxyacetonitrile was prepared by addition of excess dimethyl sulphate to the product of reaction between potassium cyanide and formalin solution at temperatures below 10°C. The oily liquid with a pyridine-like smell was extracted with ether. The ether layer was dried, the ether removed and the residue distilled at atmospheric pressure. The observed boiling point was 121°C. (Literature<sup>4</sup> 119°C at 736 m.m.).

Methyl-chloromethyl-ether was prepared by the reaction between methanol formalin and hydrogen chloride, as described by Marvel and Porter<sup>5</sup>. The observed boiling point was 53.5°C at atmospheric pressure, to be compared with 55-60°C reported by Marvel and Porter.

The spectra were recorded on a Grubb Parsons G.S. 2A double beam infra-red spectrometer calibrated with ammonia gas.

A pyrex glass vapour cell which allowed a temperature variation over the range 20°C to 200°C was used to record the vapour spectra. Matched metal cells (4.72m.m. and 9.78m.m. in length) were used to record solution spectra in chloroform, carbon tetrachloride and carbon disulphide solvents. The spectra of capillary and 0.1 m.m. thick, liquid films were also obtained.

The spectra are reproduced in figs. 1 and 2 and the frequencies given in tables 1 and 2.

## The Stable Conformations.

The type of contour obtained for vibrational bands (i.e. the PQR structure) and the P-R sub-band separation depend critically upon the moments of inertia of the molecule. These, in turn, depend upon the conformation of the mol-

ecule (fig. 3.) As one part of the molecule rotates with respect to the other the absolute and relative magnitudes of the the three principal moments of inertia change continuously: consequently the band contours and separations also change.

Molecular dimensions have not been determined for methoxyacetonitrile or for methyl-chloromethylether. Hence, from a study of similar molecules the parameters given in table 3 were chosen. With these values moments of inertia were calculated for each of the conformations given in fig. 3. (see table 4.).

The moments of inertia indicate that the molecules approximate to symmetric rotors especially for conformations near to (V). Using the theory developed by Gerhard and Dennison<sup>6</sup> the P-R separations have been calculated, for parallel type bands, from the expression,

$$\Delta \nu (P,R) = \frac{S}{\omega} \left( \frac{kT}{I} \right)^{1/2}$$

where

$$S = \frac{0.721}{(\sqrt{2} + 4)^{1/2}}, \quad \beta = (I - I_A)/I_A,$$

and

$$I = (I_B + I_C)/2.$$

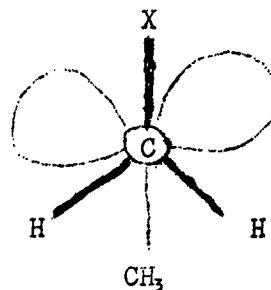
The values obtained are given in table 5, and expressed diagrammatically in fig. 4. The P-R separations found experimentally for parallel-type bands (or type A bands as described by Badger and Zumwalt<sup>7</sup>) are given in table 6.

From a comparison of the observed and calculated P-R separations it is



evident that, in both cases, the stable conformations are very close to model (V). That is the 'heavy' atom skeleton is almost planar-trans in form. This conclusion differs from that of Hayashi<sup>2</sup> who favours a gauche conformation fig. 3, II) for methyl chloromethyl-ether in the vapour state.

If the oxygen lone-pairs forming atomic dipoles are taken into account the terminal groups are seen to be staggered about the C-O bond.



In terms of bond-bond and bond-lone-pair repulsions this represents a most reasonable model.

### Vibrational Assignment.

All the fundamental modes of vibration are infra-red active. The vibrations can be conveniently divided for discussion into two groups, viz. (i) the methyl and methylene vibrations, and (ii) those associated with the COCX skeleton.

#### (i) CH Vibrations.

Tables 1 and 2 contain the assignments for these molecules made on the basis of vapour phase band contours and comparisons with related molecules.

The ranges within which the various types of methyl vibrations occur are well-known and there is little uncertainty in the assignments made in tables 1 and 2.

The assignment of frequencies to the methylene bond-stretching modes is straightforward but this is not the case with the various deformation modes since they tend to vary over large spectral regions. For example the  $\text{CH}_2$ -rocking frequency occurring at  $1176 \text{ cm}^{-1}$  in  $\text{CH}_2\text{F}_2$  is found at  $714 \text{ cm}^{-1}$  in  $\text{CH}_2\text{I}_2$ , a decrease of some 39%.

In a recent study<sup>11</sup> relations have been found between the methylene deformation frequencies in  $\text{CH}_2\text{XY}$  molecules and the electronegativity product  $\chi(X)\chi(Y)$ . These correlations have been used to predict 'group electronegativities of 3.76( $\text{CH}_3$ .O) and 3.20(CN) corresponding to frequency values centred near to 1470, 1340, 1250 and  $1,000 \text{ cm}^{-1}$  respectively for the bending, wagging, twisting, and rocking  $\text{CH}_2$  vibrations. The observed values are in good accord with

these predictions (tables 1 and 2).

The vapour spectra of the compounds are not identical in the region between  $1,400\text{ cm}^{-1}$  and  $1,300\text{ cm}^{-1}$ . Two absorption bands, one, weak, with an 'A, B' contour at  $1,397\text{ cm}^{-1}$  and the other, stronger in intensity with an almost perfect 'A' type contour at  $1324\text{ cm}^{-1}$  <sup>were</sup> observed in the spectrum of methyl chloromethylether. One complex band was observed in the spectrum of methoxyactonitrile centred at  $1364\text{ cm}^{-1}$ . The difference between the two spectra is explicable in terms of Fermi resonance between the two vibrational modes (symmetric  $\text{CH}_3$  bending and wagging  $\text{CH}_2$ ) which belong to the same symmetry class. Evidence for this is the almost equal difference in frequency between these two absorption bands in (b) and the one complex band in (a).

(b) $\text{CH}_3\text{.O.CH}_2\text{.Cl}$	1400	
(a) $\text{CH}_3\text{.O.CH}_2\text{.CN}$	1364	$36\text{ cm}^{-1}$
(b) $\text{CH}_3\text{.O.CH}_2\text{.Cl}$	1324	$40\text{ cm}^{-1}$

It is rather surprising that Fermi resonance is operative in (b) and not (a). The first overtone of the carbon-chlorine stretching vibration should occur close to  $1360\text{ cm}^{-1}$ , in the vapour spectrum of (b) and the interaction of this binary transition with the superimposed fundamentals might be the factor that results in difference in the two spectra.

(ii) Skeletal vibrations.

Three bands are expected to arise from the skeletal stretching vibrations in methyl chloromethyl ether. Two of these are best regarded as an asymmetric and symmetric stretching mode of the COC grouping,  $\nu_a(\text{COC})$  and  $\nu_s(\text{COC})$  whilst the third,  $\nu(\text{CCl})$ , is primarily localized within the CCl band. In methoxyacetonitrile there are four stretching modes,  $\nu_a(\text{COC})$ ,  $\nu_s(\text{COC})$ , and two others which can be approximately described as  $\nu(\text{CC})$  and  $\nu(\text{CN})$ .

The  $\nu(\text{CN})$  fundamental occurs near  $2250 \text{ cm}^{-1}$ , in all phases, with the very low intensity characteristic of  $\beta$ -oxygenated nitriles.

The assignment of the vibrations of the COCX chain in these molecules was facilitated by a direct comparison of the vapour spectra. Three absorption bands, of strong to medium intensity, were found in the region 1150 to  $800 \text{ cm}^{-1}$ , in the spectrum of methoxyacetonitrile. The strong absorption with an almost pure B type contour, at  $1132 \text{ cm}^{-1}$ , is assigned to the  $\nu_a(\text{COC})$  stretching vibration. The frequency of the carbon-oxygen stretching vibration in gaseous methanol is  $1030 \text{ cm}^{-1}$ . If it is assumed that the coupling between the symmetric and asymmetric modes of vibration of the COC chain results in a splitting of degenerate energy levels to give energy level pairs equally spaced on either side of the unperturbed  $\nu(\text{CO})$  vibrational level, it can be predicted that the frequency of the symmetric stretching vibration of the COC chain will be near

$$1030 - (1130 - 1030) = 930 \text{ cm}^{-1}$$

Two absorption bands, with hybrid contours, at  $932 \text{ cm}^{-1}$ , and  $890 \text{ cm}^{-1}$ , were

observed in the vapour spectrum of methoxyacetonitrile. The higher frequency band is therefore assigned to  $\nu_s(\text{COC})$  and the other to  $\nu(\text{CC})$ . This assignment is supported by the fact that replacement of the nitrile group by chlorine results in the disappearance of the  $890\text{ cm}^{-1}$  band, but does not significantly perturb the spectrum above  $900\text{ cm}^{-1}$ . This is to be expected because the chlorine atom does not differ much in mass or electronegativity from the nitrile group.

It has been shown that for molecules exhibiting rotational isomerism certain group frequencies are characteristic of particular isomeric conformations. For example in trans-monochlorinated hydrocarbons  $\nu(\text{CCl})$  varies from  $726(\text{n-propyl})$  to  $616^{-1}$ , in tert.amyl chloride, whilst the gauche frequencies range between  $645$  and  $560\text{ cm}^{-1}$  for the same series.<sup>12</sup> In the spectrum of methyl chloromethyl ether only one  $\nu(\text{CCl})$  band centred at  $646\text{ cm}^{-1}$  was detected. This comparatively high value underlines the correctness of choosing a trans-conformation. The absence of a second  $\nu(\text{CCl})$  band indicates that the gauche isomer is present to a very small extent, if at all.

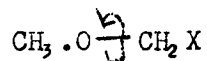
The bond-bending fundamentals of the skeleton lie below the range studied. The vibrations can be approximately described for  $\text{CH}_3.\text{O}.\text{CH}_2.\text{Cl}$  as  $\text{COC}$  bending -  $b(\text{COC})$ ,  $b(\text{OCCl})$ , both in the plane of the skeleton framework, and an out-of plane vibration which could be described as  $b(\text{OC})$  or  $b(\text{CCl})$ : for  $\text{CH}_3.\text{O}.\text{CH}_2.\text{CN}$  one has  $b(\text{COC})$ ,  $b(\text{OCC})$ ,  $b(\text{CCN})$  all in-plane and either  $b(\text{OC})$  or  $b(\text{CN})$  out-of-plane.

The corresponding frequencies are expected to be below  $500\text{ cm}^{-1}$  as is clearly shown by table 7.

Three weak bands at 838, 709, and 536  $\text{cm}^{-1}$  were observed in the spectrum of liquid methoxyacetonitrile. These can be assigned as overtone or combination bands in a number of ways. The interpretation of other combination bands observed in the higher frequency region is made more plausible if these frequencies are assigned as follows:-

$$\begin{aligned} \text{b(COC)} \sim \text{b(OCC)} &= 425 \text{ cm}^{-1} \\ \text{b(CCN)}, \text{ in plane} &= 360 \text{ cm}^{-1} \\ \text{b(CCN)}, \text{ out of plane} &= 230 \text{ cm}^{-1} \end{aligned}$$

The torsional modes of methyl groups about a C-O bond have been assigned tentatively<sup>9</sup> to bands at 160 and 230  $\text{cm}^{-1}$ . The torsional mode



would therefore be expected to have an even lower frequency.

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TABLE 1: INFRARED SPECTRUM OF METHOXYACETONITRILE

LIQUID		SOLUTIONS		VAPOUR	ASSIGNMENT.
(Raman)	Capillary	0.75mm	CCl <sub>4</sub> (0.5cm)		
3009	3008	4447 4404 4356 4269 4201 4064 3949 3640 3563 3132	3007	3018 } 3010 } 3000 }	3008+1450 = 4458 2946+1460 = 4406 3003+1370 = 1373 3008+1287 = 4295 3008+1196 = 4204 2916+1158 = 4074 2837+1115 = 3952 2256+1380 = 3636 2257+1289 = 3546 2257+ 886 = 3143
2980	2946		2940 2936	2950 } 2931 } 2908 } 2397 } 2389 }	CH <sub>2</sub> Asymmetric Stretch  CH <sub>2</sub> Symmetric Stretch CH <sub>3</sub> Asymmetric Stretch CH <sub>3</sub> Asymmetric Stretch
2914	2916		2702		CH <sub>3</sub> Symmetric Stretch
2872			2849 2832	2831 } 2822 }	1289+1370 = 2659 1460+1158 = 2618 1460+1158 = 2613 1289+1196 = 2485 1289+1158 = 2447 221196 = 2392 2x1158 = 2316 CN Stretching
2832	2837	2656 2629 2603 2464 2444 2390 2301			
	2627		2595		
	2463 2442 2389 2302 2256			2251	



TABLE 1. (Cont.)

LIQUID		SOLUTIONS		VAPOUR	ASSIGNMENT.
(Raman)	Capillary	0.75mm.	CCl <sub>4</sub> (0.5 cm)		
	2207	2206		2136	2x1115 = 2230
	2105	2105		2060	1115+1014 = 2129
	2064	2061			886+1196 = 2082
	2023	2021			886+1158 = 2044
	1757	1758	1758		2x886 = 1772
	1631	1631			1290+360 = 1650
	1466			1474	CH <sub>2</sub> Bending
	1458		1461	1467	CH <sub>3</sub> Asymmetric Bending
1455			1455	1460	
1435	1439		1437	1456	
	1380		1378	1441	
	1374			1376	CH <sub>3</sub> Asymmetric Bending
	1359		1367	1370	CH <sub>3</sub> Symmetric Bending
1363			1354	1364	
				1359	CH <sub>2</sub> Wagging
				1349	
				1294	
1285	1289		1284	1288	CH <sub>2</sub> Twisting
	1242			1279	
					1014+(240) = 1254
1185	1196		1188	1207	CH <sub>3</sub> Rocking.
				1200	
				1193	
1112	1153		1158	1161	CH <sub>3</sub> Rocking.
	1115		1117	1136	COC Asymmetric Stretch
				1128	
				1023	
	1014			1017	CH <sub>2</sub> Rocking.
				1009	
	990				1360-(360) = 1000
955	961				2256-1289 = 967
			965		

TABLE I (Cont.)

LIQUID		SOLUTIONS		VAPOUR	ASSIGNMENT
(Raman)	Capillary	0.75mm.	CCl <sub>4</sub> (0.5cm.)	CS <sub>2</sub> (0.5cm)	
914	915		919	917	
332	886		385		
404	344	838			
352	704	709			
242	536	536			
	(425)				
	(360)				
	(230)				
				937 } 922 } 924 } 399 } 890 } 832 }	COC Symmetric stretching  C-C Stretch  2x420 = 840 2x350 = 700 350+240 = 590 COC Bending CCO Bending CCN Bending

TABLE 2: INFRARED SPECTRUM OF METHYL CHLOROMETHYL ETHER.

LIQUID		SOLUTION		VAPOUR	ASSIGNMENT
Raman	Capillary	0.1mm.	CCl <sub>4</sub>	CS <sub>2</sub>	
		4459 4413 4284 4207 4091 4028 3951			2295+1470 = 4465 2958+1470 = 4428 2903+1398 = 4300 2903+1320 = 4223 2837+1278 = 4115 2837+1193 = 4030 2837+1120 = 3957
3027	2995		2994	3013	CH <sub>2</sub> Asymmetric Stretch
2980	2958		2948	2930	CH <sub>2</sub> Symmetric Stretch
2950	2943		2932	2946	CH <sub>3</sub> Asymmetric Stretch
2912	2903		2397	2901	CH <sub>3</sub> Asymmetric Stretch
2837	2837		2830	2844	CH <sub>3</sub> Symmetric Stretch
2778	2778		2770		1460+1320 = 2780
		2632			2x1320 = 2640
		2606			1460+1156 = 2616
		2464			1470+996 = 2466
2464		2438			1320+1120 = 2440
		2389			2x1193 = 2386
		2311			1397+920 = 2317
		2238			1320+920 = 2240
		2193			1278+920 = 2198
		2113			1193+920 = 2113
	2103				920+1120 = 2040
	2032				2x920 = 1840
		1345			2903-1120 = 1783
		1776			1320+350 = 1650
		1650			2995-1397 = 1598
		1576			Bending
1470	1470			1476	CH <sub>2</sub>
	1467		1461	1470	CH <sub>3</sub> Asymmetric Bending
1460	1453			1458	CH <sub>3</sub> Asymmetric Bending
				1451	CH <sub>3</sub> Asymmetric Bending

TABLE 2: (Cont.)

LIQUID		SOLUTION		VAPOUR	ASSIGNMENT
Raman	Capillary	0.1	CCl <sub>4</sub>	CS <sub>2</sub>	
1435 1398	1440 1397		1446 1396		CH <sub>3</sub> Symmetric Bending 1440) 1408 } 1400 } 1392 }
1321	1320		1317	1315	CH <sub>2</sub> Wagging 1331 } 1324 } 1317 }
1279	1273			1273	CH <sub>2</sub> Twisting 1286 } 1278 } 1270 }
1231					1397-160 = 1237 CH <sub>3</sub> Rocking 1236 } 1206 } 1198 } 1190 }
1147	1156		1156	1153	CH <sub>3</sub> Rocking 1156 } 1148 } 1138 }
1128	1120		1131	1129	COC Asymmetric Stretch 1138 } 1128 } 1121 }
998	1042 996		1043	1043 990	1450-350 = 1100 1397-350 = 1047 CH <sub>2</sub> Rocking 1092 } 1064 } 1054 } 1008 } 1000 } 993 }
920	920	805	925	917	COC Symmetric Stretch 943 } 937 } 932 }
					350+466 = 816

TABLE 2: (Cont.)

LIQUID		SOLUTION		VAPOUR	ASSIGNMENT
Raman	Capillary	0.1mm.	CCl <sub>4</sub>		
651	646		CS <sub>2</sub>	686 679 677 670	C-Cl Stretch
455	466		640		COC Bending
357	(356,				CCl Bending
177	(160)				CH <sub>3</sub> O Torsion
107					CH <sub>3</sub> O } CH <sub>2</sub> Cl Torsion

TABLE 3. DIMENSIONS OF CH<sub>3</sub>.O.CH<sub>2</sub>.X MOLECULES.

MOLECULE	C-O	COC	OCX	C-C(I)	C≡N(I)	C-Cl(II)
CH <sub>3</sub> .O.CH <sub>2</sub> .CN	1.42	110°	111°	1.47	1.16	-
CH <sub>3</sub> .O.CH <sub>2</sub> .Cl	1.42	110°	112°	-	-	1.74

TABLE 4. CALCULATED MOMENTS OF INERTIA AND ROTATIONAL  
CONSTANTS OF CH<sub>3</sub>.O.CH<sub>2</sub>.X MOLECULES.(a) CH<sub>3</sub>.O.CH<sub>2</sub>.CN

Conformation	I <sub>A</sub>	A	I <sub>B</sub>	B	I <sub>C</sub>	C
I	53	0.53	166	0.17	219	0.13
II	41	0.68	224	0.13	270	0.10
III	28	0.99	157	0.18	175	0.16
IV	38	0.75	266	0.11	343	0.08
V	17	1.65	321	0.09	338	0.08

(b) CH<sub>3</sub>.O.CH<sub>2</sub>.Cl

Conformation	I <sub>A</sub>	A	I <sub>B</sub>	B	I <sub>C</sub>	C
I	63	0.45	161	0.17	224	0.13
II	51	0.55	205	0.14	244	0.12
III	23	1.20	147	0.19	161	0.18
IV	59	0.47	242	0.12	329	0.09
V	14	2.02	304	0.09	318	0.09

TABLE 5: CALCULATED P,R SEPARATIONS OF PARALLEL-TYPE BANDS ( $\Delta\nu$ ).

(a)  $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CN}$

CONFORMATIONS	I	II	III	IV	V
$\Delta\nu$ (P,R) $\text{cm}^{-1}$	11	17.9	21.5	16.1	13.9

(b)  $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{Cl}$

CONFORMATIONS	I	II	III	IV	V
$\Delta\nu$ (P,R) $\text{cm}^{-1}$	20.4	18.0	20.9	15.5	13.5

TABLE 6: OBSERVED P,R SEPARATIONS OF PARALLEL-TYPE BANDS.

$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CN}$	$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{Cl}$
$\left. \begin{array}{l} 1349 \\ 1359 \\ 1364 \end{array} \right\} 15 \pm 1$ $\left. \begin{array}{l} 1279 \\ 1288 \\ 1294 \end{array} \right\} 15 \pm 1$ $\left. \begin{array}{l} 1193 \\ 1200 \\ 1207 \end{array} \right\} 14 \pm 1$ $\left. \begin{array}{l} 1123 \\ 1128 \\ 1136 \end{array} \right\} 13 \pm 1$ $\left. \begin{array}{l} 1009 \\ 1017 \\ 1023 \end{array} \right\} 14 \pm 1$ $\left. \begin{array}{l} 924 \\ 922 \\ 937 \end{array} \right\} 13 \pm 1$	$\left. \begin{array}{l} 1408 \\ 1400 \\ 1392 \end{array} \right\} 16 \pm 1$ $\left. \begin{array}{l} 1331 \\ 1324 \\ 1317 \end{array} \right\} 14 \pm 1$ $\left. \begin{array}{l} 1286 \\ 1278 \\ 1270 \end{array} \right\} 16 \pm 1$ $\left. \begin{array}{l} 1156 \\ 1148 \\ 1138 \end{array} \right\} 18 \pm 1$ $\left. \begin{array}{l} 1121 \\ 1120 \\ 1138 \end{array} \right\} 17 \pm 1$ $\left. \begin{array}{l} 686 \\ 679 \\ 677 \\ 670 \end{array} \right\} 16 \pm 1$

TABLE 7: FREQUENCIES OF SKELETAL VIBRATIONS.

MOLECULE	b(COC)	b(OCC)	b(XCC)	Ref.
$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_3$	414	-	-	9
$\text{CH}_3 \cdot \text{O} \cdot \text{CHO}$	325	-	-	10
$\text{CH}_3 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$	303	429	-	10
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$	-	427	-	13
$\text{CN} \cdot \text{CH}_2 \cdot \text{CN}$	-	-	582	14
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CN}$	-	-	531	15
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{F}$	-	-	415	16
$\text{HO} \cdot \text{CH}_2 \cdot \text{CN}$	-	410	-	17



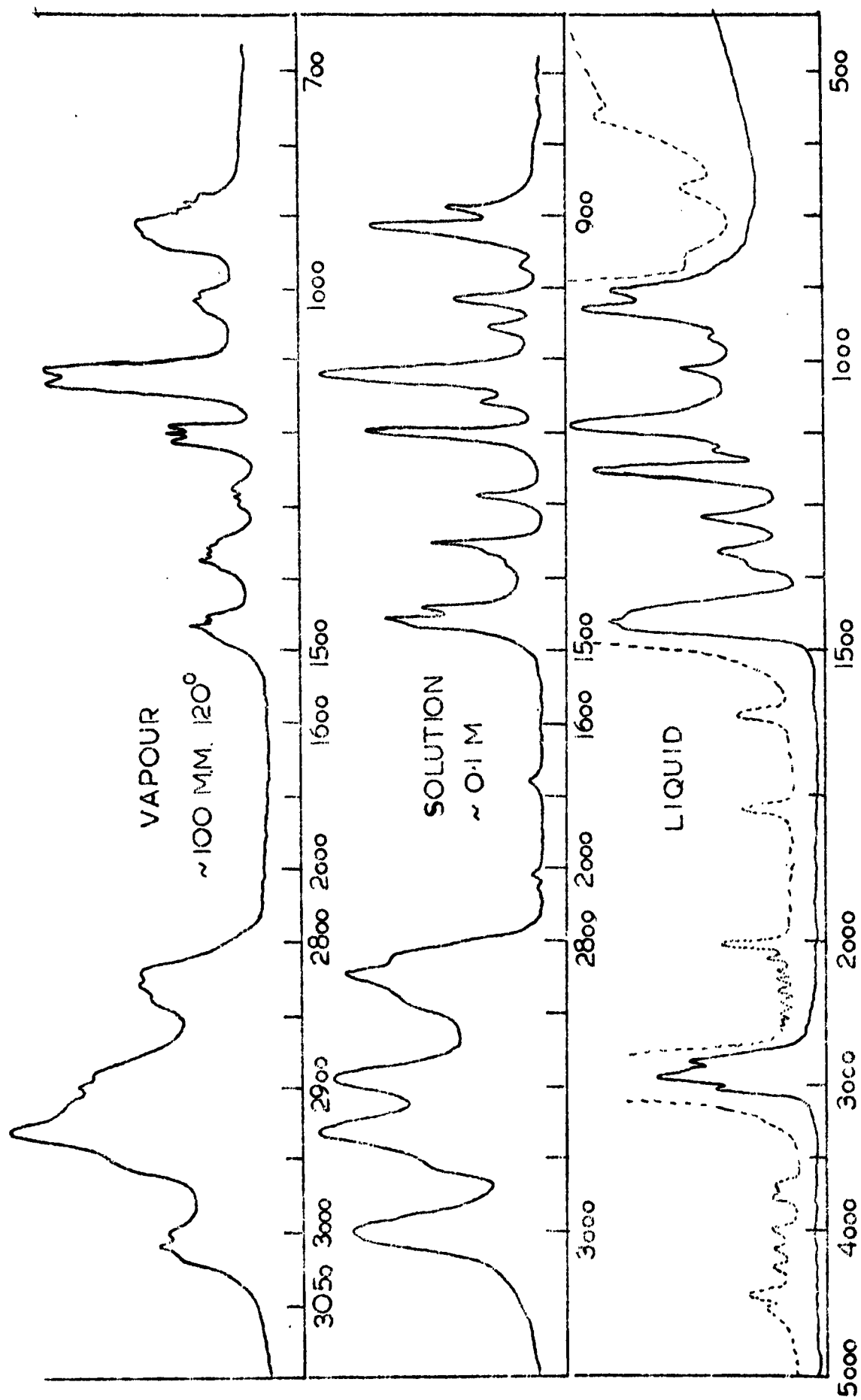


FIG.1  $\text{CH}_3\text{CHO}$

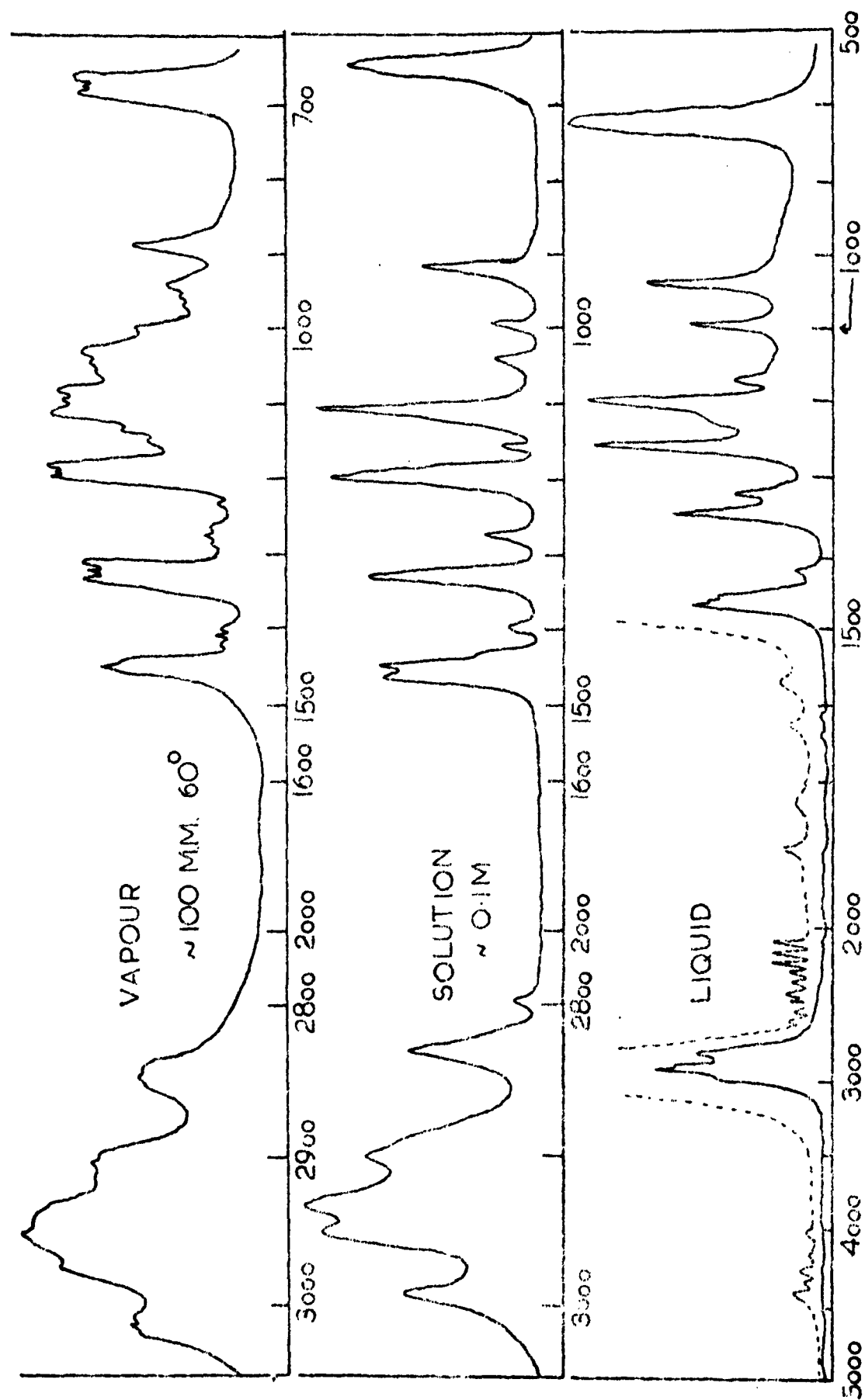


FIG 2  $\text{CH}_3\text{OCH}_2\text{Cl}$

FIG. 3 CONFORMATIONS OF  $\text{CH}_3\text{OCH}_2\text{X}$  MOLECULES.

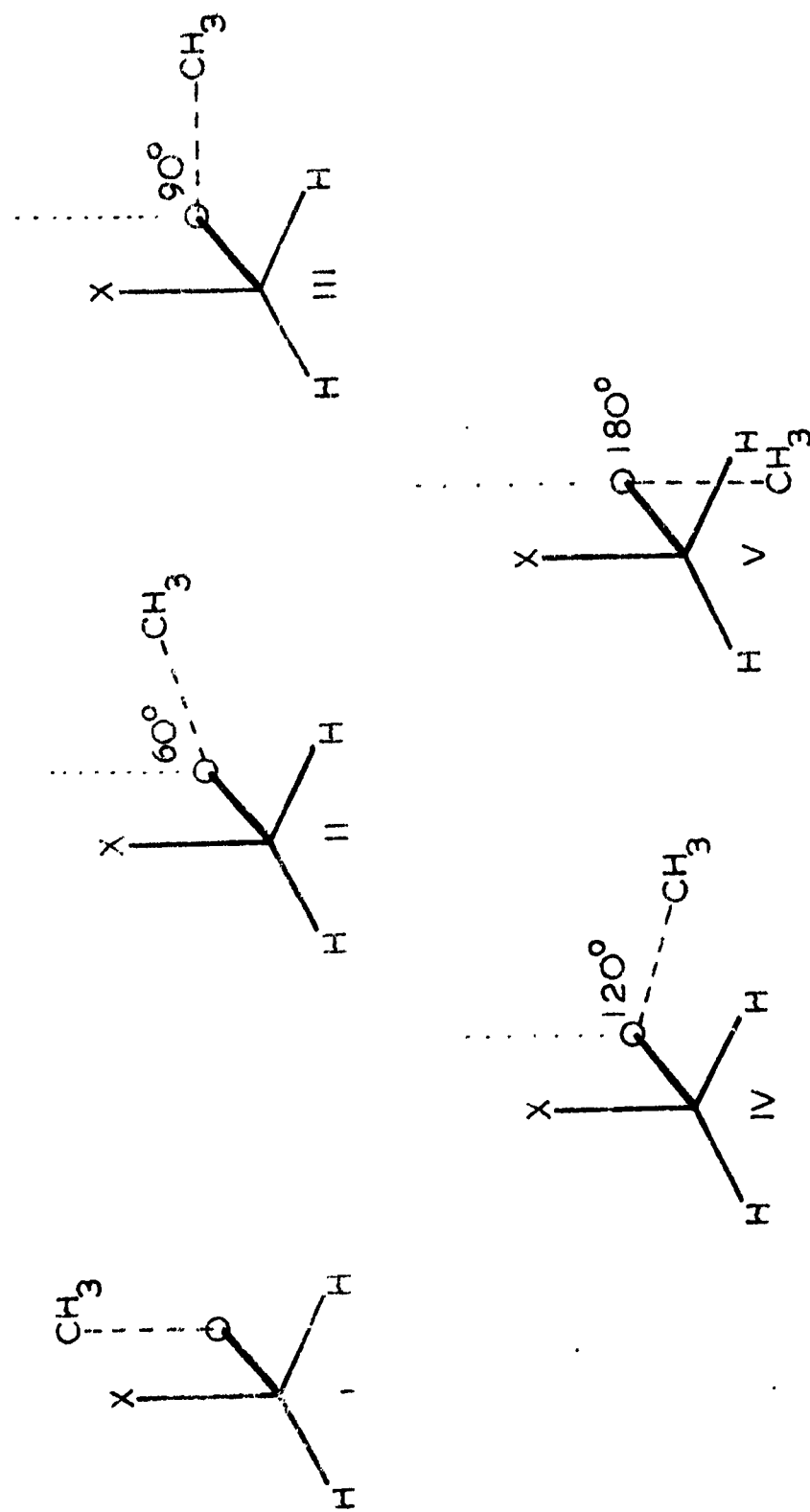


FIG. 4A

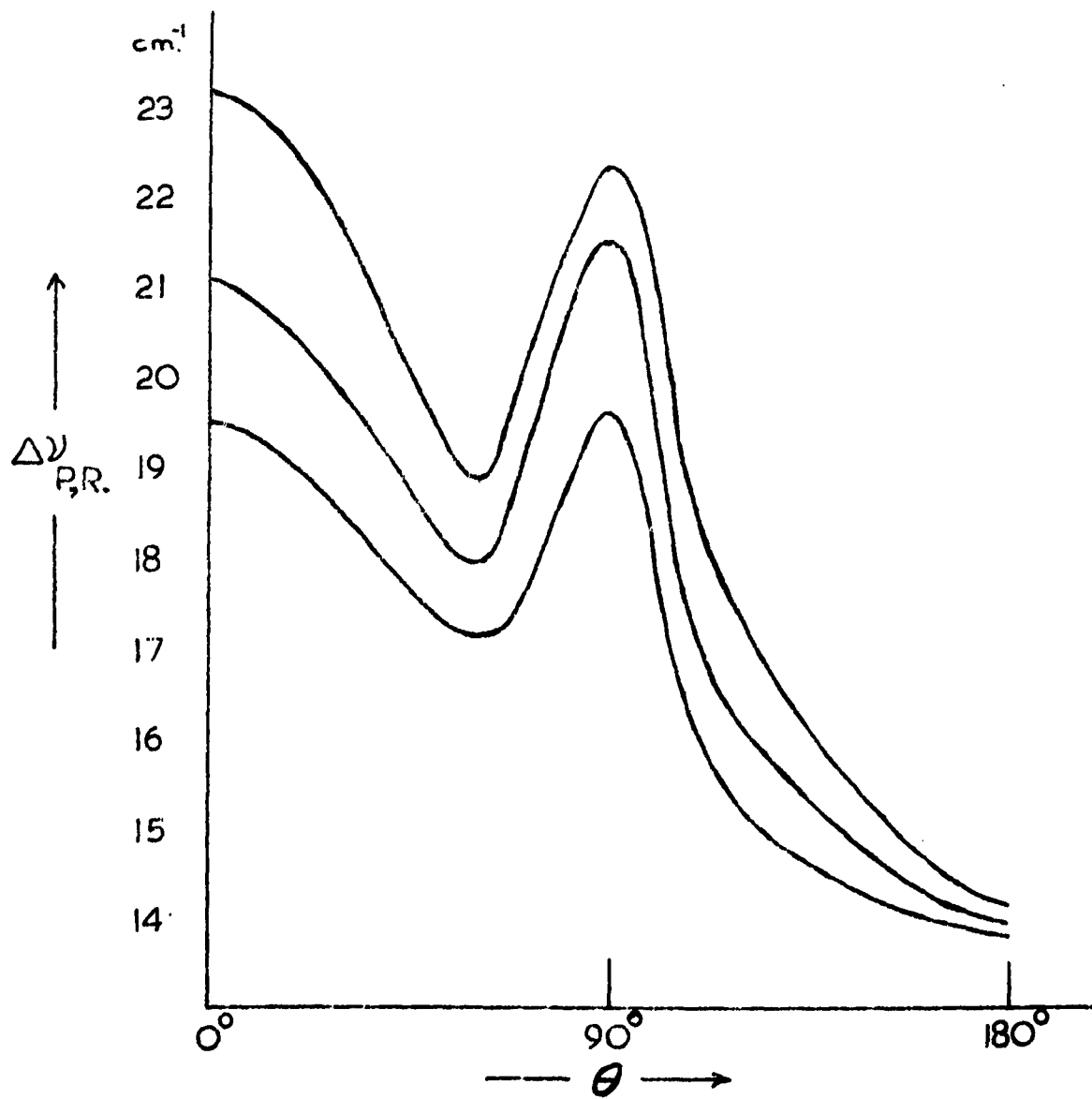
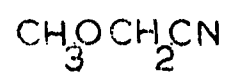
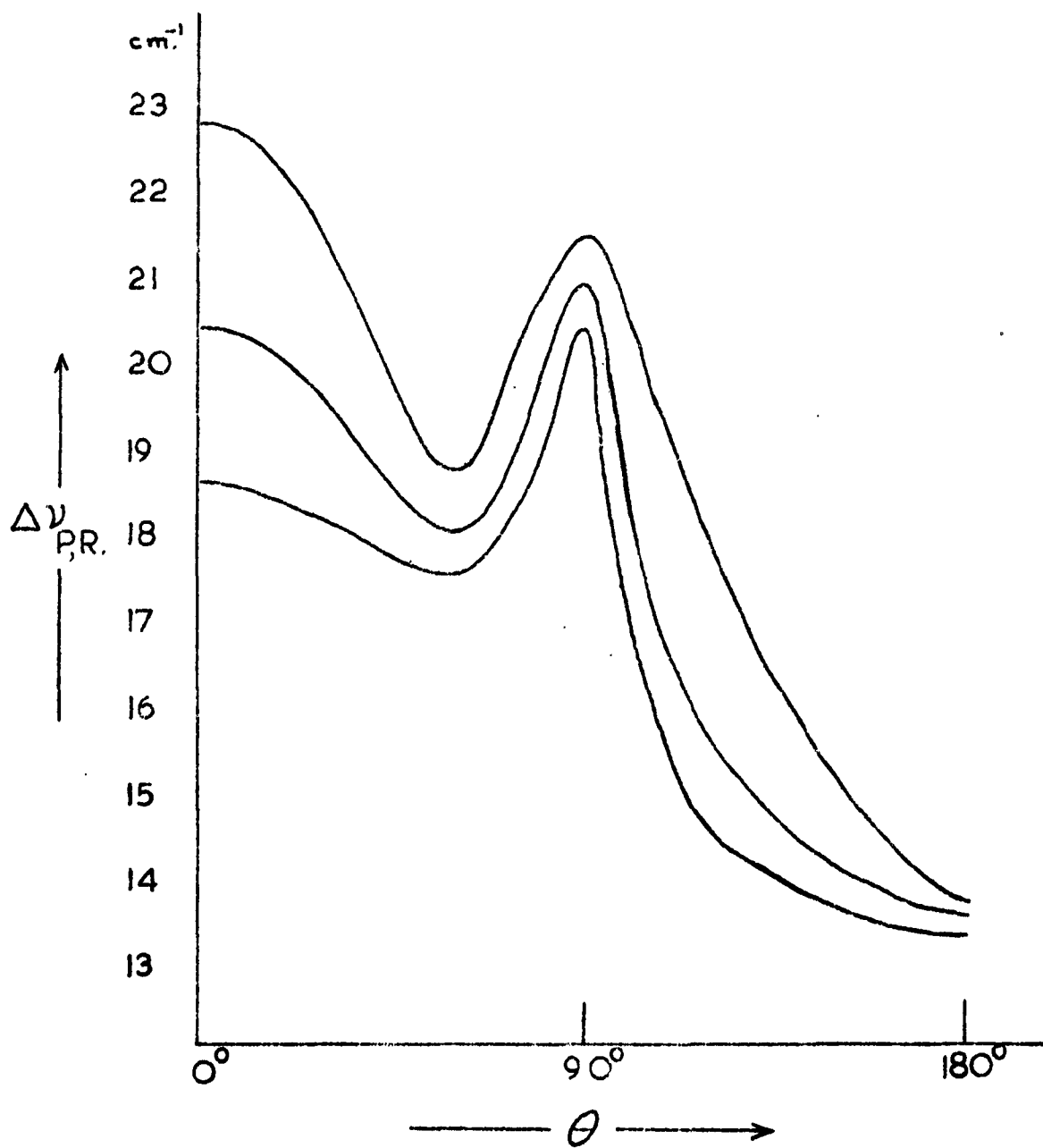
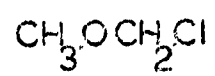


FIG 4B



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